Low Temperature Processing of Ultra-Pure Cellulose Fibers into Nylon 6 and Other Thermoplastics

Rod Jacobson, Dan Caulfield, Karl Sears, and John Underwood

Introduction

Techniques for compounding and injection molding ultra-pure cellulose fibers into nylon 6 and other thermoplastics will be described. Low temperature compounding (LTC) is a technique that provides a processing route to utilize ultra-pure cellulose fiber as a reinforcement in resins with melting points greater than 220°C. In particular, nylon 6 has a melting point of 221°C which is well above the commonly stated belief that cellulose fiber should not be compounded above the 200°C benchmark. By understanding and utilizing the viscosity shear heating effects of cellulose fiber/nylon 6 composite systems, the LTC method provides high quality composite pellets for injection molding. Low temperature injection molding (LTIM) is a technique that will be described which provides a means of producing ASTM standard test samples for mechanical property evaluation. Other recent publications (1-3) have described the mechanical properties of cellulose fiber/nylon 6 composites. This discussion will focus on LTC and LTIM methods of producing the cellulose fiber/nylon 6 composite pellets and test samples.

Background and Objectives

In 1984, Klason, Kubàt and Strömvall (4) reported on the use of cellulose flour and cellulose fibers as reinforcement in polyamides. The researchers were unsuccessful with the higher melting point polyamides, such as nylon 6. The composite materials exhibited severe discoloration and pyrolytic degradation of the cellulose fiber reinforcement. Although there was some success with the use of nylon 12 (melting point range 176° to 180°C), their overall view toward the use of cellulose as a reinforcement in high melting point polyamides was unfavorable, and this view has persisted for over 15 years.

The objective of this research was to develop a stable process for compound ultra-pure cellulose fibers into polyamides. This has been a difficult procedure and has taken years of trial and error to understand the viscosity shear heating effects associated with compounding cellulose into high-melting point engineering thermoplastics. The evolution of the low temperature compounding (LTC) technique is ongoing, and the ongoing development of new process stabilizers for cellu-

Jacobson:
President, A-J Engineering Co., LLC, Madison, WI
Caufield:
Research Chemist, USDA Forest Products Lab., Madison, WI
Sears:
Principal Scientist, Specialty Fibers
Underwood:
Director of Marketing Development, Rayonier - Performance Fiber Division, Jesup, GA

lose-polyamide composites will help facilitate the commercial use of these new materials for industrial applications.

Ultra-Pure Cellulose Fibers and Fiber Pelletizing

The high purity cellulose fibers produced by Rayonier, Performance Fiber Division described in this section are the following:

- hardwood prehydrolyzed kraft (HPK) fiber with 98.0 percent alpha-cellulose,
- mercerized hardwood prehydrolyzed kraft (MHPK) fiber with 99.5 percent alpha-cellulose, and
- softwood prehydrolyzed sulfite (SPS) fiber with 98.0 percent alpha-cellulose.

A major obstacle to compounding high purity cellulose fibers into engineering and other thermoplastic resins is the materials handling problems associated with low bulk density materials. The consistent delivery of fibers into an extruder with currently available feed hopper systems is critical if cellulose fiber as a reinforcement in engineering resins is to be accepted by the polymer industry. A consistent feed rate of material into an extruder is essential for good dispersion, accurate fiber loading levels, minimized surging of the material at the die face, process stability (i.e., torque characteristics), and ease of pelletizing the resultant composite materials. Cellulose fiber pelletizing techniques have been developed to address the problems of materials handling on a commercial development scale.

Never-dried cellulose fibers were shipped to the Forest Products Laboratory and stored in a 36°F 50 percent relative humidity, cold room prior to fiber pelletizing to prevent biological growth and subsequent fiber degradation. The never-dried fibers are shipped at 39 to 40 percent solids for proper mixing and pelletizing characteristics (i.e., prior R & D efforts have determined these levels for our particular pelletizing system). A Hobart batch mixer with a 60-liter capacity is used in the first step to pelletizing the never-dried fibers. Batch sizes metered out for mixing the cellulose with additives ranging in size from 50 to 70 lb. depending on which fiber type is being pelletized. HPK fibers have a weight average fiber length (WAFL) of 0.82 mm and generally 70 lb. of material is metered for blending. The SPS fibers have a weight average fiber length (WAFL) of 1.52 mm and generally 60 lb. of material is metered for blending due to the increase in fiber length, which results in different blending characteristics. The MHPK fibers have a weight average fiber length (WAFL) of 0.82 mm and generally 50 lb. of material is metered for blending due to the change in fiber surface characteristics and decrease in bulk density as a result of the mercerization process. Each never-dried cellulose fiber type has slightly different characteristics associated with the blending and pelletizing process. This section will describe the general outline for producing never-dried cellulose fiber pellets and not the specific characteristic's for each cellulose fiber type.

During the blending stage, a Hercules carboxymethylcellulose 7H4F (CMC) viscosity modifier is added into the Hobart mixer to change the rheology of the never-dried pulp and prevent de-watering of the never-dried fibers during the pelletizing process. The CMC is added in the range of 0.003 to 0.005 by weight of the never-dried fiber depending on the fiber type, and blended for 15 minutes in the Hobart mixer to assure good dispersion of the CMC throughout the cellulose fiber suspension. The high purity cellulose fibers are then vacuum-conveyed out of the Hobart mixer and are ready for the cellulose pelletizing stage.

A Kahl Pellet-Press (laboratory scale model #175) is used for pelletizing the never-dried fibers blended with the CMC additive. The Kahl Pelletizer has a horizontal pellet die plate with dual rotating roll-mills that provide the downward force required to press the cellulose fibers through the horizontal die plate. A 6 mm die plate with a 4 to 1 pressway was used to produce early versions of the cellulose fiber pellets for industrial compounding trials. As a result of these earlier industrial trials, a 3 mm die plate with a 6 to 1 pressway is currently being utilized to produce all three types (i.e., HPK, MHPK, and SPK) of cellulose pellets for industrial compounding trials. The smaller pellets feed more accurately through existing material feed hopper systems and are delivered more uniformly to the extruder feed-throat or to a side-feeder attachment. In the case of the MHPK pulp fibers, the shift to the 3-mm die has provided improved cellulose pellet quality due to the slight increase in pressure dynamics with the 3-mm die and a reduction in “fiber networks” which mechanically interlock some of the cellulose pellets together and reduce the desired free-flow characteristics of the pellets.

After the Kahl pelletizing process, the cellulose fiber pellets are oven dried at 105°C to reduce the moisture content to below 0.5 percent and packaged hot for shipment. The loose packing density of 3 mm pellets as packaged for shipping is approximately 217 kg/m^3. If the pellets are opened and exposed to moist ambient conditions before the twin-screw extrusion trials, then care should be taken to re-dry the pellets before extrusion. The cellulose is hygroscopic and can easily gain 8 to 10 percent moisture. This moisture will cause foaming and off gassing of the composites during compounding.

Twin-Screw Extrusion and Compounding

Pre-Blended Feed-Throat Method of Compounding

In the initial stages of this research, composites were prepared by pre-blending cellulose and matrix thermoplastic and feeding this pre-blended mixture to the feed-throat of the twin-screw extruder. With careful control of the melt-temperature of the composite by adjusting rotational screw-speed and cooling rates of the various zones, it was possible to prepare composites of high-melting thermoplastics reinforced with cellulose. The mechanical properties of typical cellulose fiber-reinforced nylon composites prepared by the pre-blended feed-throat method have been reported in references 1 and 2. These initial pre-blended feed-throat experiments indicated that careful temperature control was necessary for successful compounding and that methods for minimizing the unnecessary exposure of cellulose to high temperatures was beneficial. This realization led to development of introducing cellulose fibers into the molten polymer stream using a side-stuffer attachment on the twin-screw.

Low Temperature Extrusion Processing Protocol Using a Side-Stuffer

Low temperature compounding (LTC) of cellulose pulp fiber compositesin high melting thermoplastics is a unique compounding method for producing cellulose reinforced engineering thermoplastic composites using a twin-screw equipped with a side-stuffer. Careful attention to this compounding sequence or protocol as described here in detail is required to produce high quality composites. These detailed procedures are provided to aid, and serve as a guide for, the compounding of Rayonier pulp-pellets into nylon (PA-6). The specific descriptions apply to a Davis-Standard, 32 mm, co-rotating twin-screw extruder, compounding equipment that has been used at the Forest Products Laboratory. It consists of seven heating zones and has an L/D = 36:1. Typical operating conditions include a rotational screw speed of 200 ±10 rpm and a production rate of about 11 kg/hr. of composite pellets. Use of alternate equipment is possible with appropriate modifications of screw-configurations and procedures to reproduce the temperature, pressure, and shear-mixing conditions experienced by the polymer/ cellulose fibers in the DS twin screw. The extruder is equipped with a 28 mm (screw-type)/crammer located at heater block #4 or about half of the (900 mm) distance between the feed throat and die-face. The die face is a four-hole strand die. A schematic of a typical screw configuration is shown in Figure 1.

This particular compounding method to be described has three phases: start-up conditions, a transition phase, and steady-state conditions.

Start-up Conditions

The start-up conditions for compounding cellulose pulp fibers into PA-6 are straight forward. Temperature setting of the seven heat zones are set at 232°C (450°F), which is well above the melting point of PA-6. Polymer (PA-6) is introduced at the feed-throat at a constant metered rate by an AccuRate gravity feed hopper (a typical feed-rate might be about 7 to 10 kg/hr. for this 32-mm extruder). The cellulose pellets are introduced into the melted polymer stream by the side-stuffer/crammer, which is calibrated to deliver cellulose pellets at a rate equal to one-half of the polymer feed-rate. This results in a composite blend of 33 percent cellulose and 67 percent PA-6. As cellulose is added into the polymer, the melt viscosity will begin to rise and the side-stuffer/crammer feed-rate will have to be increased slightly to counter-balance the increased extrusion melt pressure in the extruder. At steady-state conditions, the cellulose pellet feed-rate no longer requires adjustment. No additives are necessary. Figure 2 shows a schematic of a viscosity shear heating curve for cellulose reinforced PA-6 composite production. Figure 3 is a schematic of the temperature settings associated with start-up conditions.

Transition Phase

The transition phase of LTC is the most dynamic and turbulent region in the progression to-

Segment #	Element* used	Segment #	Element* used	Segment #	Element* used
1	FF 0.75	11	FF 1.50	21	FF 1.00
2	FF 1.50	12	FF 1.50	22	FK 1 .50
3	FF 1.50	13	FF 1.50	23	BK 1.50
4	FF 1.50	14	FF 1.50	24	FF 1.50
5	FF 1.50	15	FF 1.00	25	FF 1.00
6	FF 1.50	16	FF 1.00	26	FF 1.00
7	FF 1.25	17	FF 100	27	FF 1.00
8	FK 1.00	18	FF 1.00	28	FF 1.00
9	BK 0.50	19	FF 1.00	29–31	(3) FF 0.75
10	FF 1.50	20	FF 1.00	32	Screw caps

*Elements: FF = Forward feed; CK = Cross kneader; BK = Back kneader. Units = L/D ratio.

Figure 1 . ~ Typical screw configuration used during compounding.

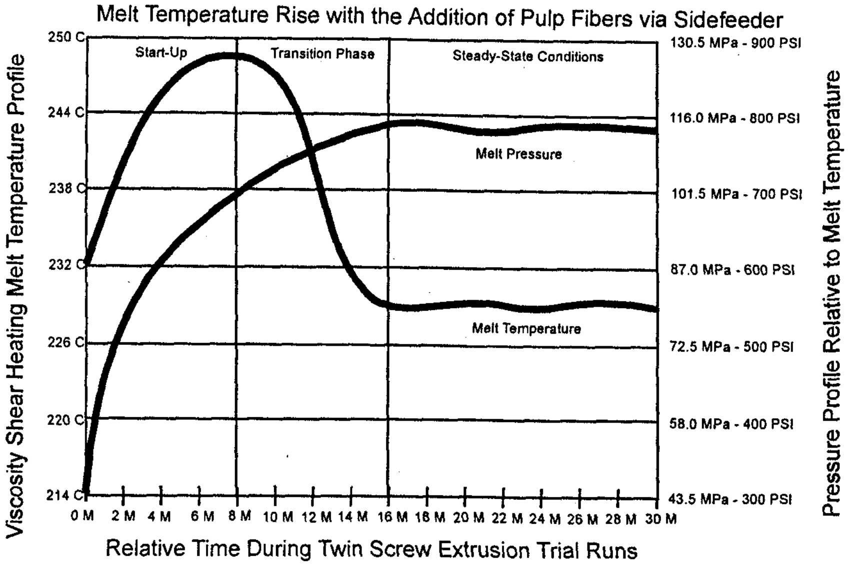

Figure 2. ~ *Viscosity shear heating curve for cellulose reinforced PA 6, showing the three phases: start-up, transition and steady state.*

ward steady-state conditions and high quality cellulose reinforced engineering thermoplastic composites. With the continued addition of cellulose pulp fibers via the sidefeeder/crammer, the melt viscosity will increase substantially. This increase in melt viscosity will cause the melt temperature and torque load (i.e., percent load) on the extruder to increase dramatically. The cellulose pulp fibers will experience a rapid increase in temperature and the composite melt temperature in the extruder may rise to over 260°C (500°F) within 5 to 6 minutes. As the temperature nears the thermal decomposition temperature for cellulose, there is a rapid decrease in the composite strand strength,

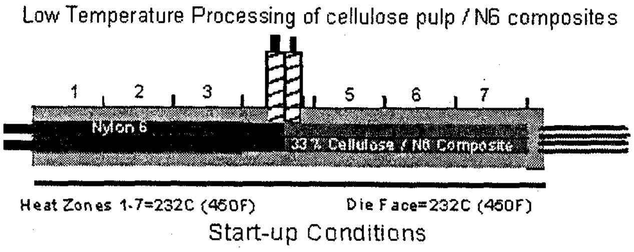

Figure 3. ~ *Schematic ofthe temperature settings associated with start-up conditions.*

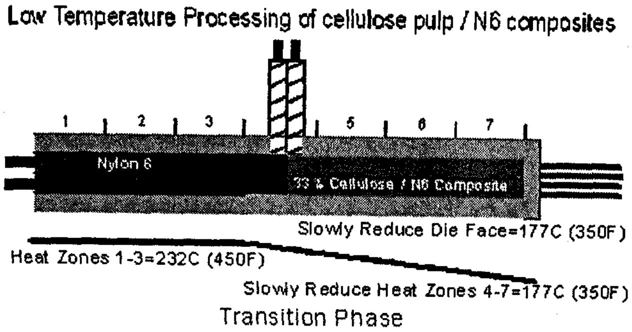

Figure 4. ~ *Schematic of the temperature heat profiles associated with transition phase conditions for nylon 6.*

surface quality, and the potential for scorching and severe discoloration (brown color) of the composites.

At this point, the temperature setting of zones 4-7 should be immediately lowered to 218°C (425°F) and then 204°C (400°F) within 5 to 6 minutes. At the 204°C (400°F) temperature settings, the rapid rise in the melt temperature should peak and possibly start to come down in temperature. Now the temperature setting on zones 4-7 should be "gradually reduced" by 5° to 7°C (10° to 15°F) to start to control the melt temperature throughout the transition phase. A representative temperature profile of the screw during the transition phase of the extrusion is shown in Figure 4. As zones 4-7 are used to control the composite melt temperature, the composite strand quality and color will begin to improve as the temperature settings move down through the 193°C (380°F), 188°C (370°F), 182°C (360°F) temperature range. At 177°C (350°F) temperature reading, the composite strands should lighten in color and begin to appear cream colored, strand strength will improve, and surface quality will improve. Continue the gradual reduction in temperatures of zones 4-7 until steady-state conditions are obtained and the compounding/processing conditions come to equilibrium.

Steady-State Conditions

The viscosity shear heating of the polymer composite is a critical element during the LTP compounding sequence. At steady state conditions, the twin screw extruder is at equilibrium and the temperature settings of the seven heating zones have gradually been transformed into a step function. Zones 1-3 are set at 232°C (450°F), while zones 4-7 are set at or near 149°C (300°F) depending on screw configuration, rpm setting, and die face conditions. These settings (or temperature readings) are below the melting point of the polymer, and the extruder may appear cool to the touch, but, in fact the shear heating in the twin screw maintains the composite above that temperature, and the excess damaging shear heating is dissipated through the extruder's cooling coils. The melt temperature of the cellulose/PA-6 composites should now be in the range of 218° to 227°C (425° to 440°F) for continuous operation.

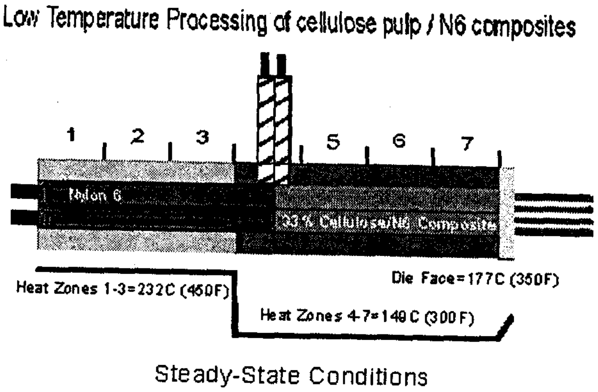

Figure 5. ~ *Schematic of the temperature heat profiles associated with steady-state conditions for nylon 6.*

In addition to the heating zones, the particular screw configuration used and rpm settings help provide the viscosity shear heating required to plasticize the composite. The compounding screws convey and mix the composites through a continuously cooled extrusion barrel (i.e., zones 4-7). By controlling zones 4-7, the melt temperature of the extrudate can be maintained and controlled to prevent scorching and charring of the composite. At steady-state conditions, the composite strand quality will have improved from the transition phase of chocolate brown to a cream-colored composite. The composite strands are water cooled and chopped into pellets. The temperature profile of the screw at steady-state conditions is shown in Figure 5.

As the compounding trial comes to an end or enough material has been collected for injection molding or other trials, zones 4-7 should be raised to the start-up conditions of 232°C (450°F) before the cellulose feed is terminated. When the zone temperatures in 4-7 reach approximately 204°C (400°F), the cellulose can be turned off and PA-6 continued. A purge material can then be utilized to

Table 1. ~ *Mechanical properties ofPP and PA-6 composites.*

	Tensile strength	Flexural strength	Tensile modulus	Flexural modulus	Notched Izod	Unnotched Izod
	- - - - - - - - (MPa)	- - - - - - -	- - - - - - - (GPa)	- - - - - - -	- - - - - - - -(J/m)	- - - - - - - -
Polypropylene	27.6	28.7	1.39	1.39	16.1	556.4
PP + 33% wood flour	33.1	49.3	3.38	3.19	18.7	75.4
Nylon 6 (PA-6)	60.2	64.2	2.75	2.38	24	746.3
PA-6 + 30% wollastonite	62.7	105.7	6.51	6.27	25.8	173.9
PA-6 + 33% glass fiber	111.2	146.7	8.02	7.55	45.9	406.1
PA-6 + 33% HPK fiber	86.5	121.6	5.71	5.88	25.3	318.3
PA-6 + 33% SPS fiber	81.9	113.9	5.35	5.45	25.1	247.2

clean the composite material from the twin screw extruder.

Caution: If there is an interruption in the flow of either PA 6 or cellulose pellets during steady-state operation, this will result in the material freezing in the extruder and an overload of the torque reading (i.e., percent load), which will end the compounding sequence. At this time, the low temperature settings should be immediately set to start-up conditions until the screws will rotate again. It is suggested that if the composite melt is interrupted in this fashion that the extruder die-face be cleaned of any charred composite material and the compounding sequence returned to the original start-up conditions.

Injection Molding

Low temperature injection molding (LTIM) of cellulose pulp fiber/nylon-6 composites is a unique injection molding method for producing cellulose reinforced engineering thermoplastic composites. Careful attention to this injection molding process is required to produce high quality composites. The size of the injection molding equipment in comparison to the molded part is critical to producing high quality parts (i.e., too much time at temperature can cause discoloration and darkening).

Although larger injection molding equipment has been used in an industrial setting trial, the detailed procedures, described here are specific to the 33-ton Cinncinati-Milicron injection molding machine at FPL using a standard ASTM test specimen mold - tensile, flexural, and Izod impact test samples. The Cinncinati-Milicron 32 mm reciprocating screw injection molder with an L/D of 20:1 has three electrically heated barrel zones, nozzle temperature control, with a mold heater capacity of 121°C (250°F). When injection molding composite pellets, the barrel sections should be set at 232°C (450°F) and the nozzle at 227°C (440°F), while the mold heater setting should be at 121°C (250°F) or higher to facilitate a good surface finish (i.e., no orange peel/splay marks) and promote the flow of the material. Injection speeds during the molding process should be high (3.6 m/sec.) to push the molten material forward (quickly) and enhance the surface finish. Moderate pack and hold pressures of 1,000 psi are adequate to start the injection molding process. The injection molding conditions involved a packing pressure of 167 MPa and a holding pressure of 160 MPa. The screw speed was 200 rpm with an injection speed of 91 mm/sec.

The mechanical properties measured by ASTM standard methods on LTP prepared composites molded by LIMP methods are presented in Table 1. In general the mechanical properties for the 33 percent cellulose fiber reinforced PA-6 are intermediate between the wollastonite and glass-fiber reinforced PA-6 composites. The cellulose fiber reinforced polyamide composites are also approximately twice as strong and twice as stiff as wood-flour filled polypropylene and have better notched and unnotched Izod toughness than the wood flour/PP composites.

Conclusions

It is possible to extrude composites of cellulose fibers in high melting engineering thermoplastics (like PA-6 and PA-6,6) by twin-screw extrusion techniques using either pre-blended feed-throat methods or side-stuffer methods that utilize control of temperature resulting from viscosity shear-heating. This method is best facilitated by side-stuffer introduction of pelletized cellulose fibers into the polymer melt. By using the low-temperature processing as described in this paper, where the effects of over-heating due to shear-heating are minimized, uniform composites are prepared which show little discoloration and no charring. The composite pellets so prepared from cellulose fiber reinforced PA-6 can be injection molded into parts or test specimens that exhibit mechanical properties that are generally intermediate between wollastonite filled and glass-fiber reinforced materials. The density, color, and surface appearance of these injection-molded materials appear suitable for some automotive applications. Additional processing advantages arising from the use of cellulose fiber reinforcement instead of glass-fiber are its lower density and its less abrasive nature in processing equipment.

Acknowledgments

The authors wish to acknowledge the following individuals for their assistance in this research: Jeff Stauffacher for his careful laboratory work in the preparation of composites; Joe Ignatious, President of Quantum Mechanix, Barneveld WI, for his generous loan of the alternator cover injection-mold; and the personnel of FPL's Engineering Mechanics Laboratory, Bill Nelson, Lori Schroeder and Marshall Begel for composite property evaluations.

References

1. Sears, K., R. Jacobson, D. Caulfield, and J. Underwood. 2000. Composites containing cellulosic fibers and methods of making and using the same. U.S. Patent (Published International Application WO 00/21743), PCT Gazette, Apr. 20.
2. Sears, K., R. Jacobson, D. Caulfield, and J. Underwood. 2001. Reinforcement of engineering thermoplastics with high-purity wood cellulose fibers. *In:* Proc. of the Sixth International Conf. on Woodfiber-Plastic Composites. Forest Products Society. May 15-16, Madison, WI.
3. Caulfield, D., R. Jacobson, K. Sears, and J. Underwood. 2001. Woodpulp fibers as reinforcements for high-melting engineering thermoplastics for 'under-the-hood' automotive applications. In: Proc. PPS-17 The Polymer Processing Society. May 21-24, Montreal, Canada.
4. Klason, C., J. Kubàt, and H.E. Strömvall. 1984. Intern. J. Polymeric Materials. 10:159-187.

Sixth International Conference on Woodfiber-Plastic Composites

May 15–16, 2001
The Madison Concourse Hotel
Madison, Wisconsin

Sponsored by the USDA Forest Service in cooperation with the
ACS Cellulose, Paper and Textile Division, the American Plastics Council,
the Market Development Alliance of the FRP Composites Industry,
the University of Wisconsin, the University of Toronto,
and the Forest Products Society.

Forest Products Society
2801 Marshall Court
Madison, WI 53705-2295
phone: 608-231-1361
fax: 608-231-2152
www.forestprod.org